



# Polymer Pyrolysis Kinetics

*Vadim D. Knyazev*

Research Center for Chemical Kinetics

Department of Chemistry

The Catholic University of America

Washington, DC 20064



- Pyrolysis of polymers is directly related to flammability and thermal stability of plastics.
- Combustion of polymers is, generally, a gas-phase process with gaseous fuel supplied by the decomposing solid or liquid polymer. Understanding of polymer pyrolysis is key to understanding and controlling the chemistry and physics of polymer combustion and flammability.
- Existing abundant experimental data on polymer pyrolysis stimulate development of microscopic models based on the chemistry of the elementary reactions involved.
- Kinetic modeling has become a valuable and widely used tool for design and control of a multitude of different chemical processes.
- Over the past decade, considerable efforts have been directed at kinetic modeling of decomposition of polymers.

However...

- Fundamental knowledge of rate constants of elementary reactions is of key importance to the success of such modeling. This information is largely unavailable for the reactions involved in polymer decomposition.

## Backbone C-C scission

- **Gas phase rate:**  $k = (10^{16} - 10^{17}) \times \exp(-348 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}$

This rate expression requires unrealistically high temperatures for initiation of polymer decomposition.

$$k = 1.0 \text{ s}^{-1} \text{ at } T = 1069 - 1136 \text{ K}$$

- At typical temperatures of experiments on polyethylene pyrolysis this gives very low values of rate constants:

$$k = 10^{-11} - 10^{-10} \text{ s}^{-1} \text{ per C-C bond, at } T = 400 \text{ }^{\circ}\text{C} (673 \text{ K})$$

(or  $10^{-8} - 10^{-7} \text{ s}^{-1}$  per a  $\text{C}_{1000}$  PE chain)

- To explain low-temperature (350 – 450 °C) pyrolysis of polyethylene and similar polymers, one needs to assume that initial C-C bond scission occurs with rates that are significantly higher than the rates of the gas phase alkane decomposition.

## Backbone C-C scission

### Recent work by Nyden, Stoliarov, and coworkers (2004):

- Thermal decomposition of polyethylene, polypropylene, and polyisobutylene was studied using Reactive Molecular Dynamics (RMD). Bulk polymer melt conditions were used in the model.
- Several reaction types were included in these simulations, including C-C bond scission.
- These authors reported activation energies for polymer C-C scission (40 – 190 kJ mol<sup>-1</sup>) that are significantly lower than those of alkanes in the gas phase (~ 350 kJ mol<sup>-1</sup>).
- In-depth analysis of polyisobutylene decomposition demonstrated that C-C scission activation energy decreases with the polymer chain length, from 240 kJ mol<sup>-1</sup> for PIB4 to 170 kJ mol<sup>-1</sup> for PIB150.
- Authors' explanation:
  - nonbonding interactions induce torsional and angular stresses; these stresses are larger in larger polymer molecules.
  - These stresses are partially relaxed when the polymer chain is broken, thus reducing the barrier for C-C backbone scission.

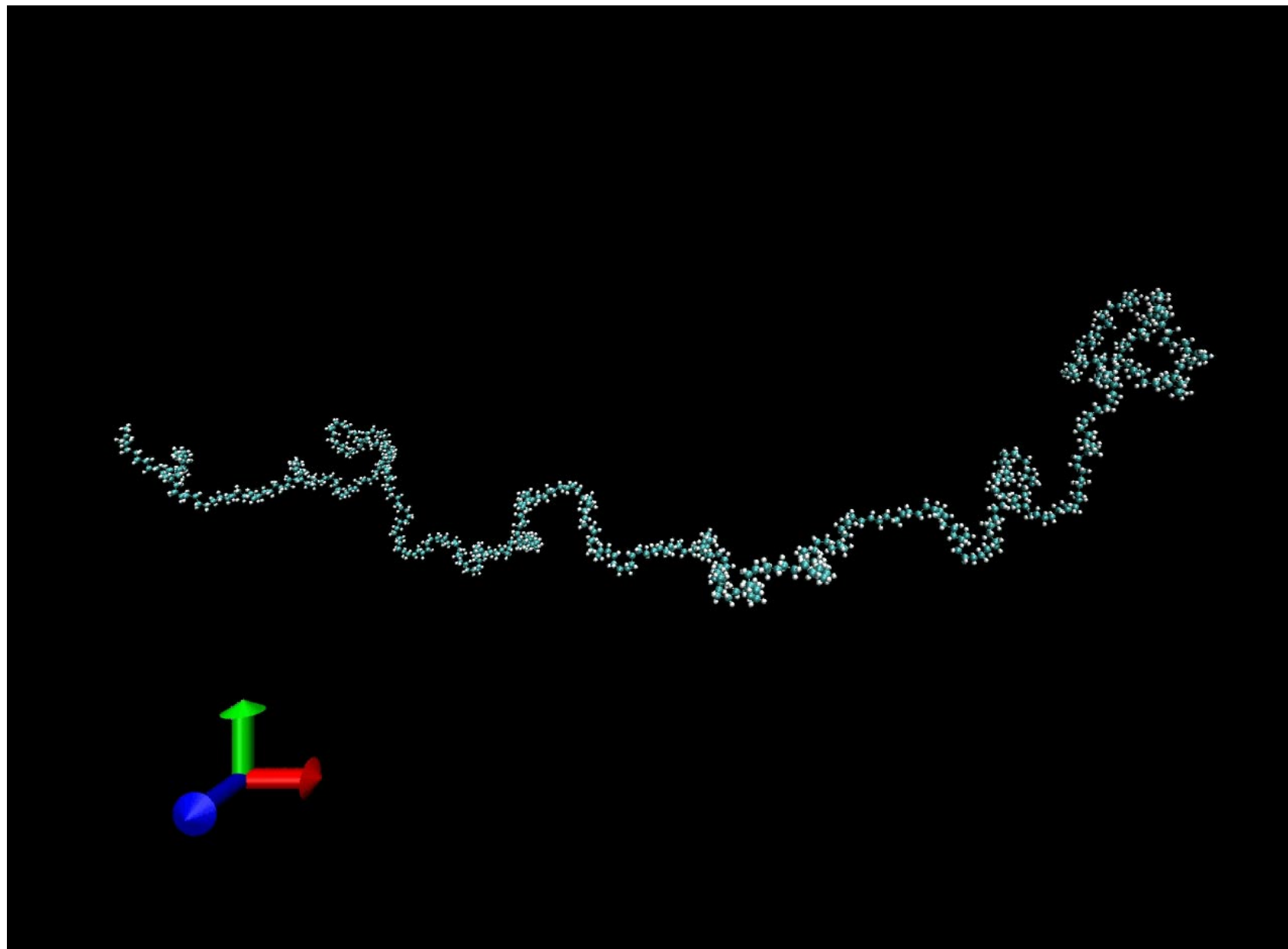
## Backbone C-C scission

### Current work:

- C-C backbone scission in polyethylene in the gas phase was chosen as the model system.
- Transition State Theory predicts decomposition rates similar to those of smaller alkanes in the gas phase.
- The initial goal of the work was to compare reaction rates obtained in classical Molecular Dynamics calculations with those resulting from Transition State Theory (or RRKM theory) and to analyze any resulting differences.
- Software used: GROMACS, All-atom force field with Morse function for C-C bonds ( $348 \text{ kJ mol}^{-1}$  bond energy).
- Transition State Theory and RRKM calculations were performed using the same potential energy surface and classical densities of states, to emphasize differences due to the use of MD vs TST and those due to macromolecular nature of the species studied.

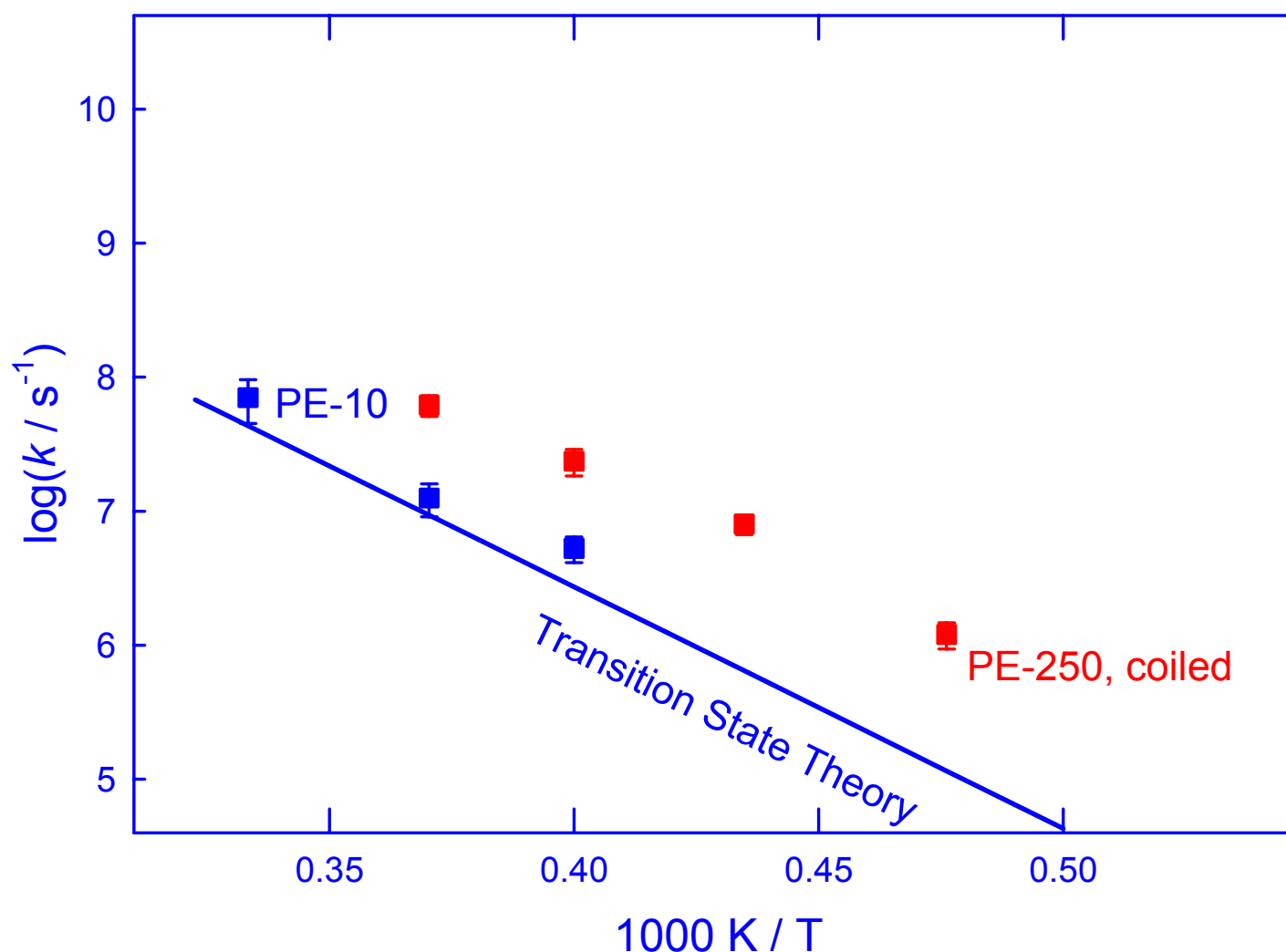
# Backbone C-C scission

- Example of MD run with C-C bond dissociation:



## Rate constants: MD vs TST, dependence on the chain length

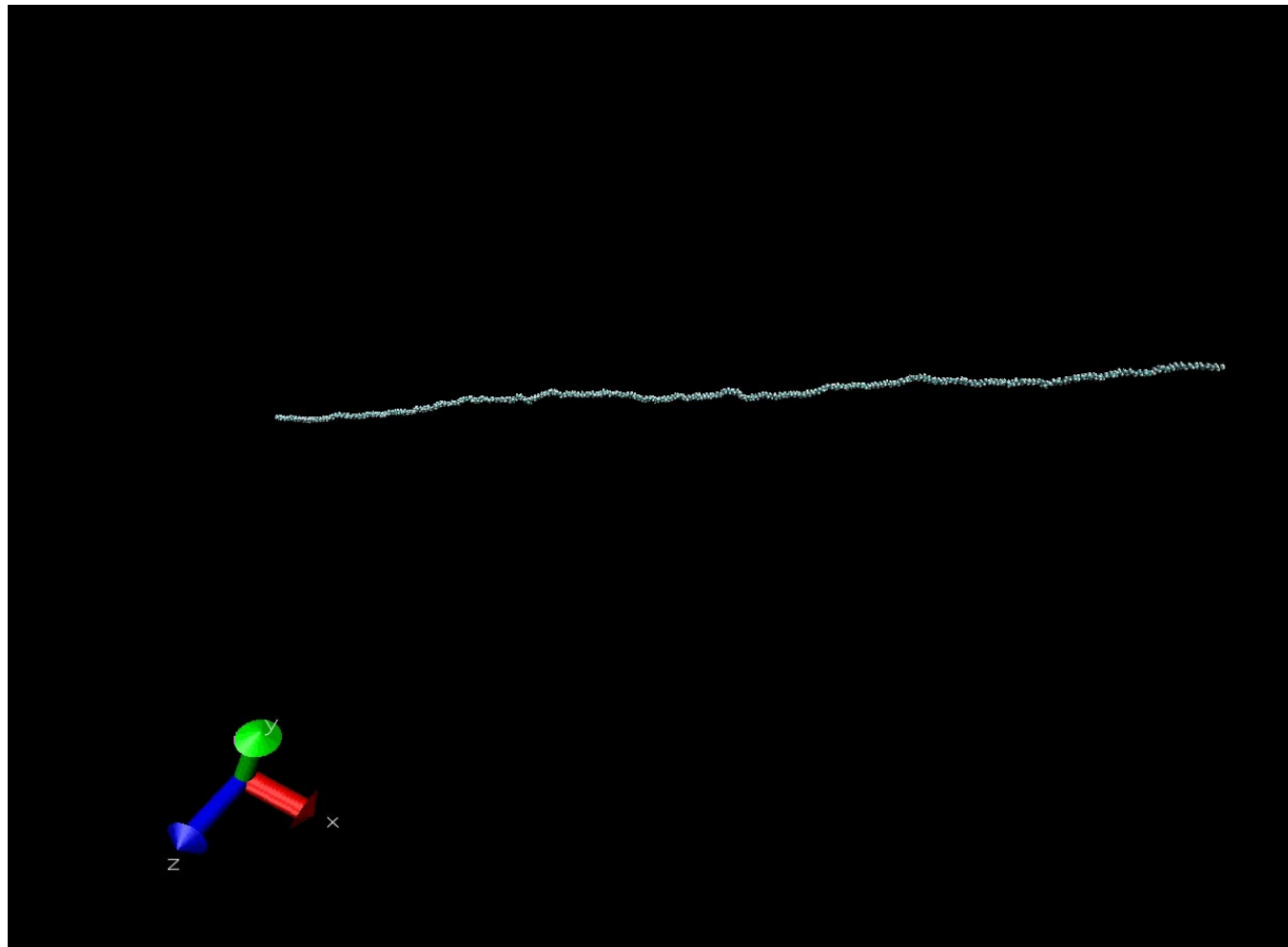
- Rate constants are larger than predicted by TST
- Rate constants (per C-C bond) increase with the chain length
- Activation energy is similar to that predicted by TST, which agrees with the small alkane gas phase activation energy.



## Rate constants: MD vs TST, dependence on the chain length

- Rate constants increase even further if the PE-250 chain is forced to remain extended.

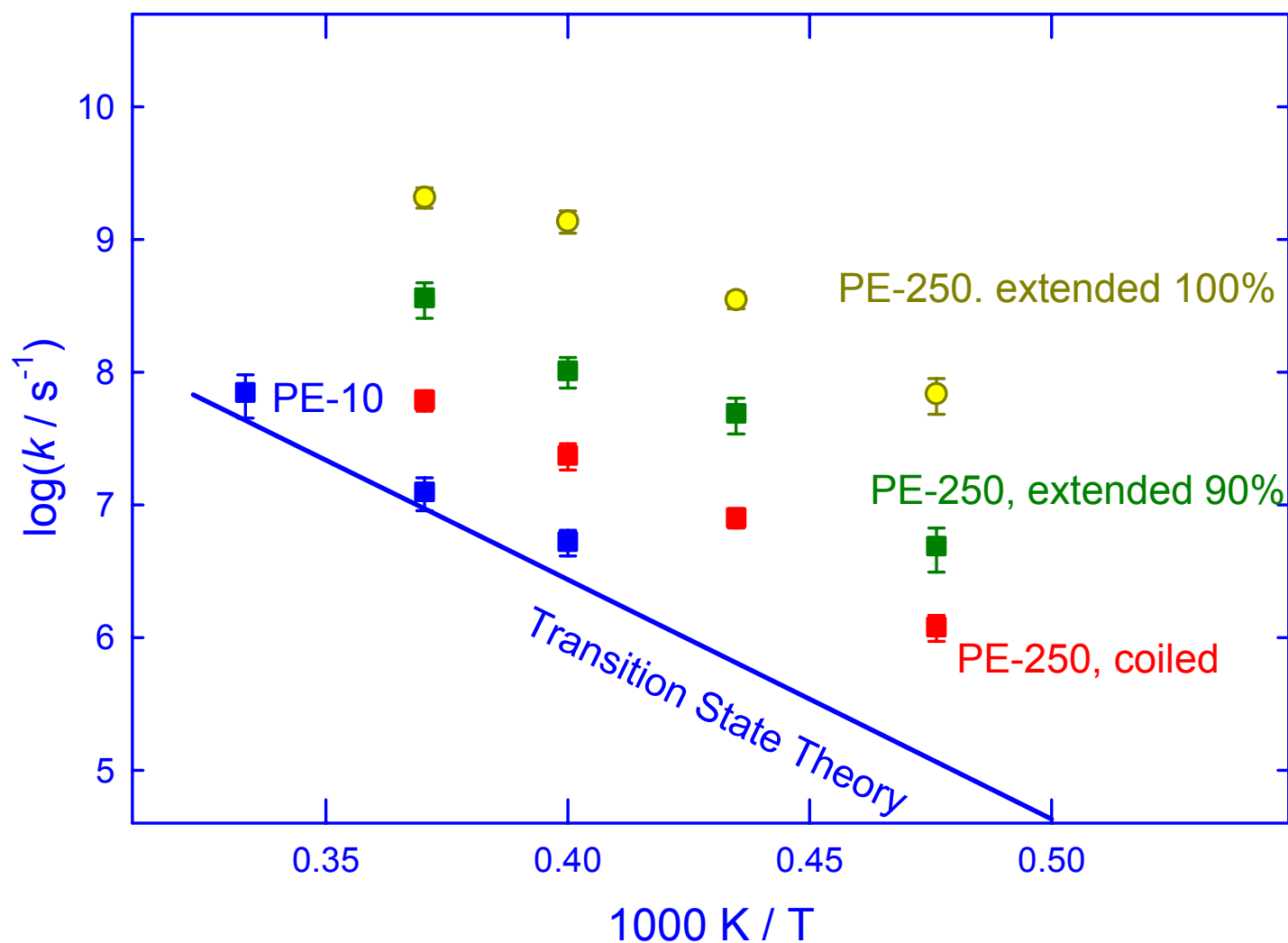
Example of MD simulation of a molecule extended by 100% (ends are fixed at the distance equal to 100% of the distance in the linear minimized configuration):





## Rate constants: MD vs TST, dependence on the chain length

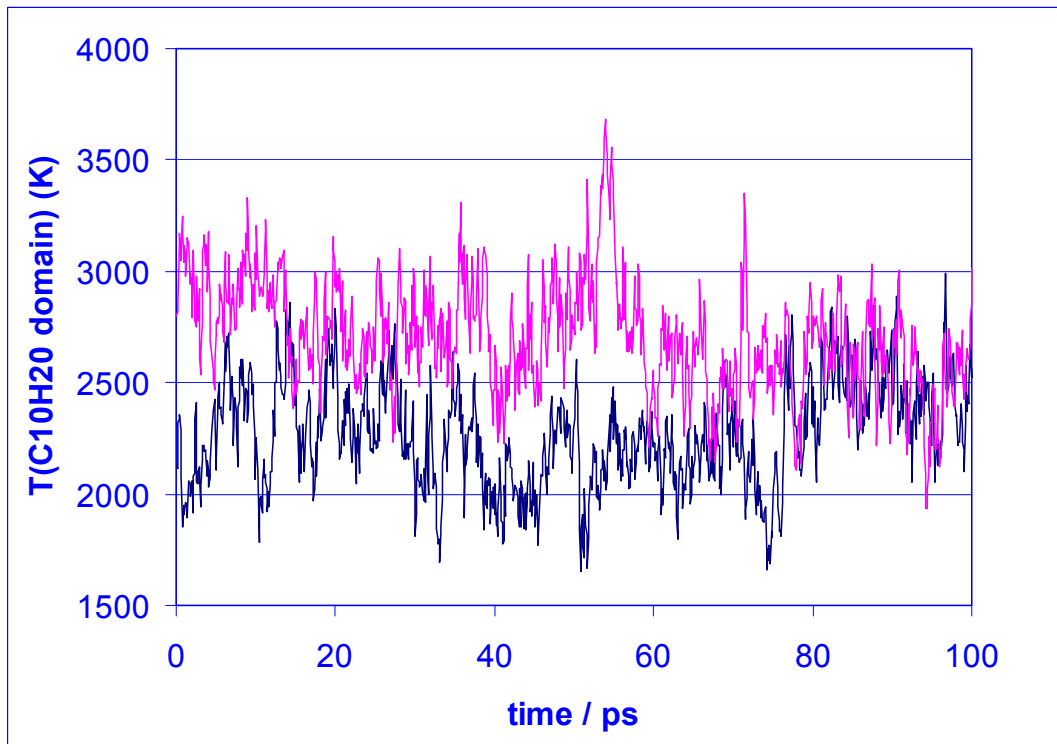
- Rate constants increase even further if the PE-250 chain is forced to remain extended.



## Possible explanations of the rate constants increase with the chain length and change in the chain configuration

### 1. Nonuniform distribution of local temperatures.

Classical RRKM calculations were performed using a model of effective “reactive domains” – segments of a macromolecule within which intramolecular energy transfer is fast compared to the time of the reaction. The resultant rate constants are a factor of 1 – 10 larger than those obtained in TST calculations, depending on the size of the “reactive domain.” However, this effect alone is insufficient to explain the rate constant values observed in MD simulations.



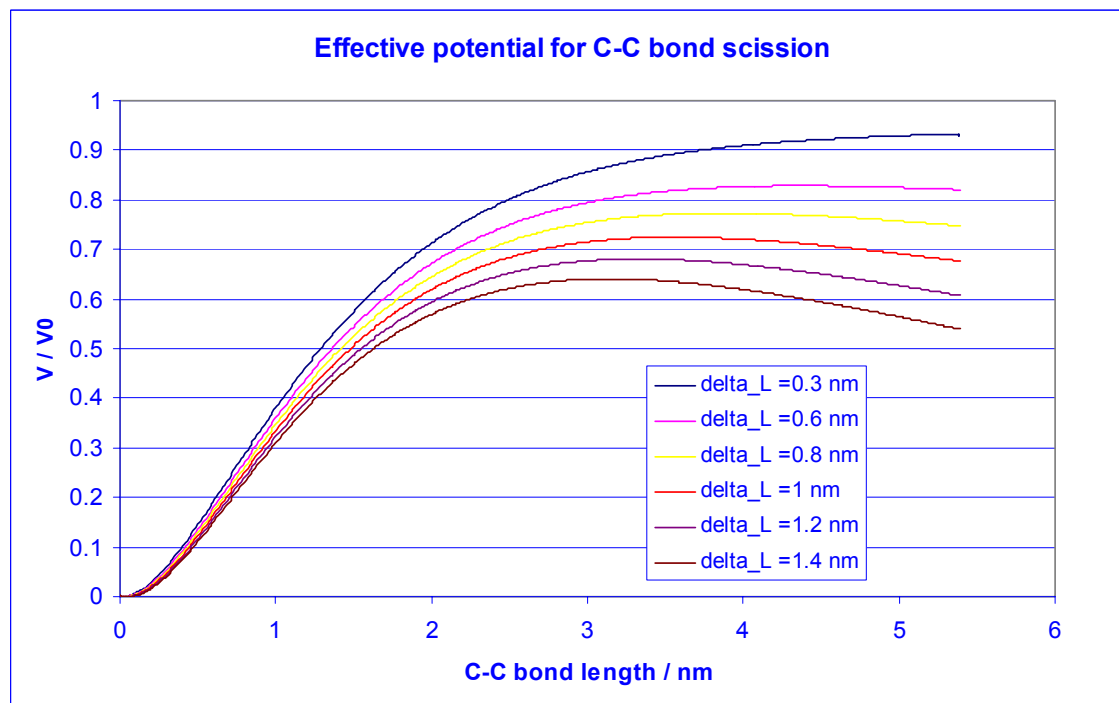
*Example of a time dependence of the local temperature of a C<sub>10</sub>H<sub>20</sub> “reactive domain.” Local temperature fluctuations reach into hundreds of K. Since  $k(T_{\text{LOCAL}})$  dependences are non-linear, local temperature fluctuations result in an increase in the rate constant.*

## Possible explanations of the rate constants increase with the chain length and change in the chain configuration

### 2. Chain stretching induced by bending vibrations.

Stretching of a polymer chain by an external force is known to reduce the barrier for backbone scission (e.g., Crist et al., 1982).

Even if each individual bond is stretched by a small amount, the whole chain (or even a segment of a chain) can accumulate relatively large amounts of potential energy. Then, when one bond starts dissociating, other bonds contract and thus release the stored energy, which becomes available for overcoming the dissociation barrier.



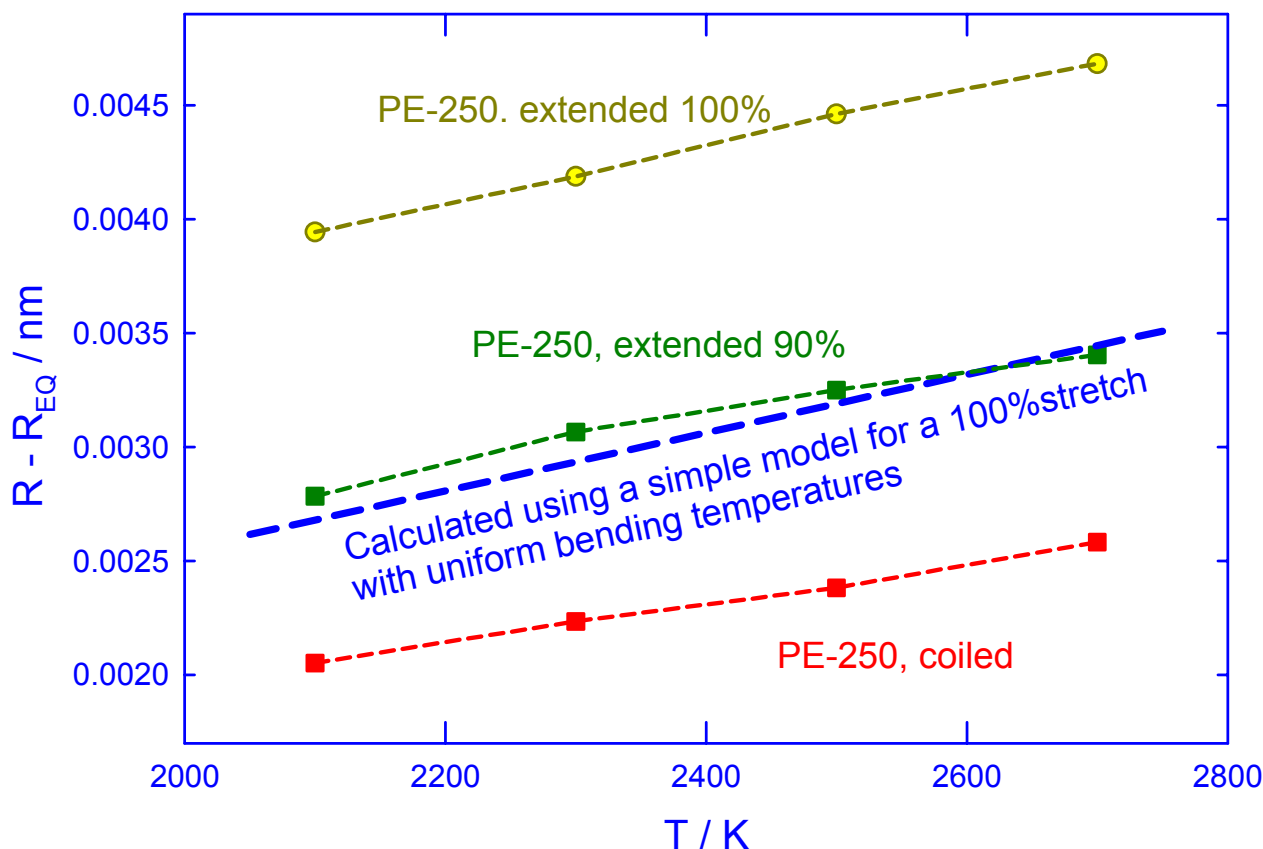
*Effective potential for scission of an individual C-C bond in a stretched chain of PE-100.*

*Different lines correspond to different lengths of stretch (0.3 – 1.4 nm)*

## Possible explanations of the rate constants increase with the chain length and change in the chain configuration

### 2. Chain stretching induced by bending vibrations.

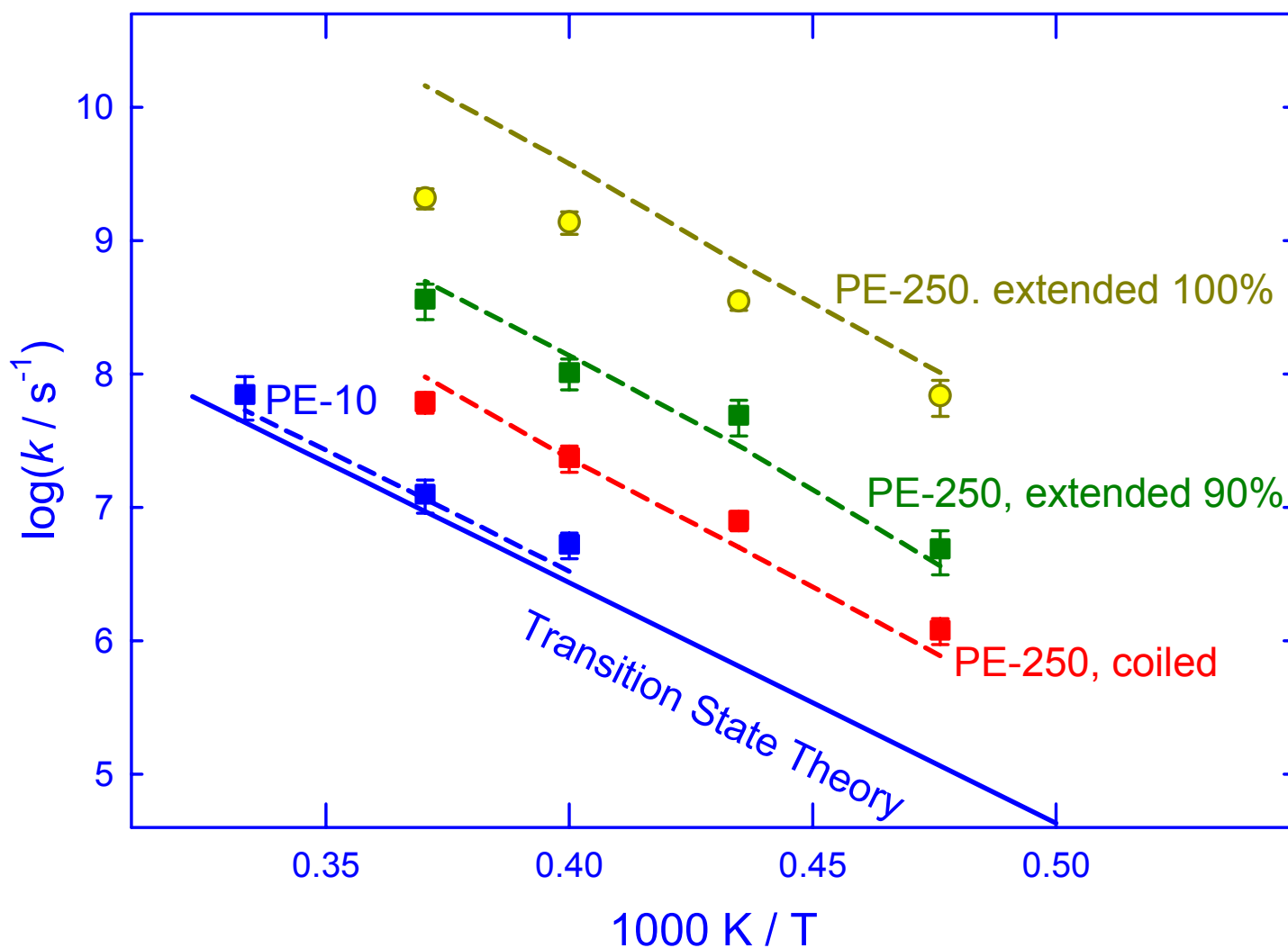
- For a one-dimensional chain with harmonic C-C bonds (and no bending degrees of freedom) the average C-C bond length will not depend on the degree of vibrational excitation.
- For the three-dimensional PE-250 chain with all harmonic stretches, however, the average C-C bond length increases with temperature.



*Dependence of average C-C bond stretch relative to equilibrium distance as a function of temperature for three different chain configurations of PE-250.*

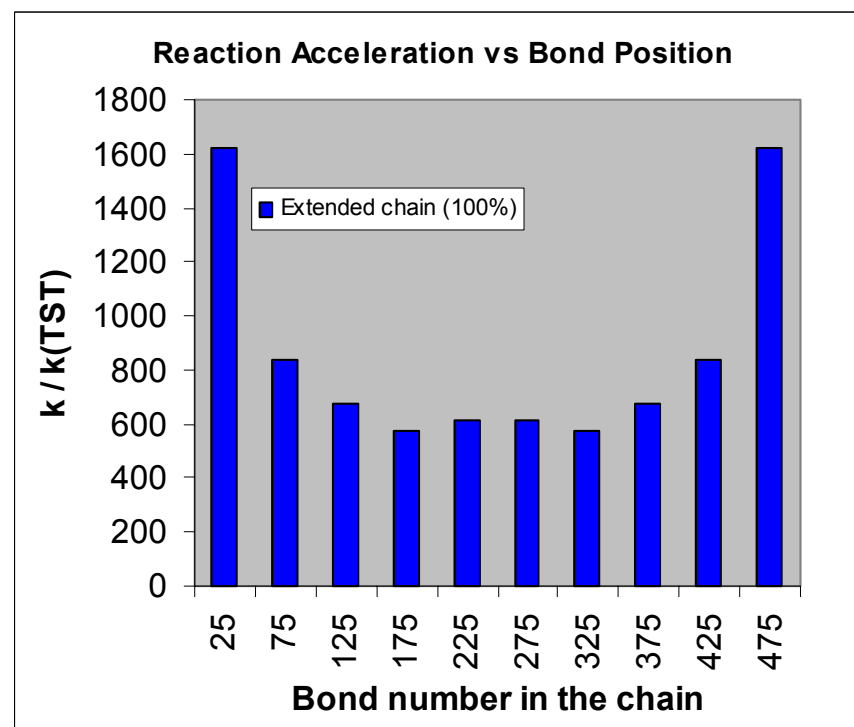
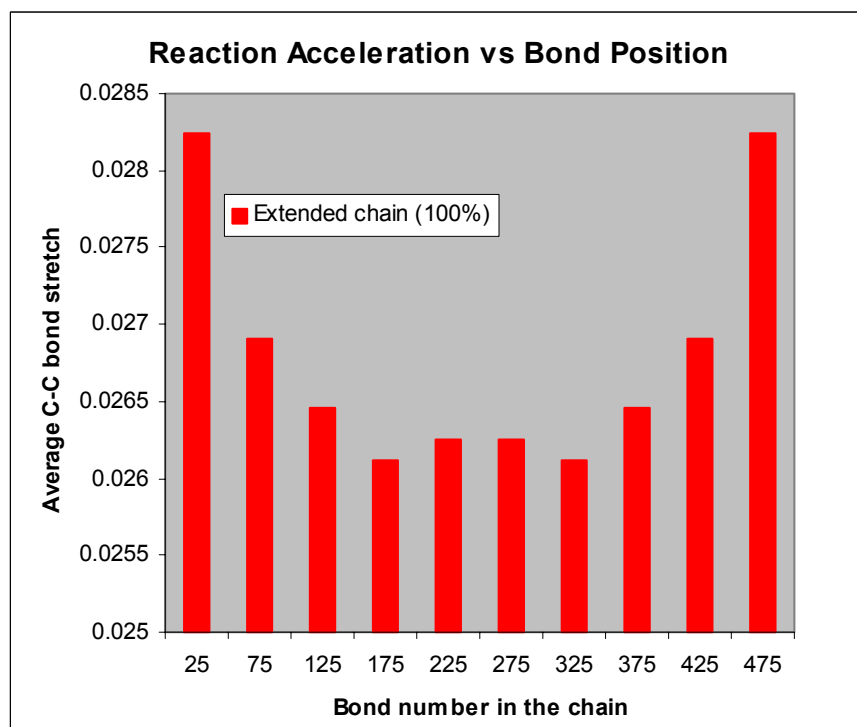
## Possible explanations of the rate constants increase with the chain length and change in the chain configuration

2. Chain stretching induced by bending vibrations.
  - Corrections to TST-based rate constants (dashed lines on the plot) were obtained with reaction barriers calculated using MD-based average bond stretches and “effective chain length” of 72 bonds.



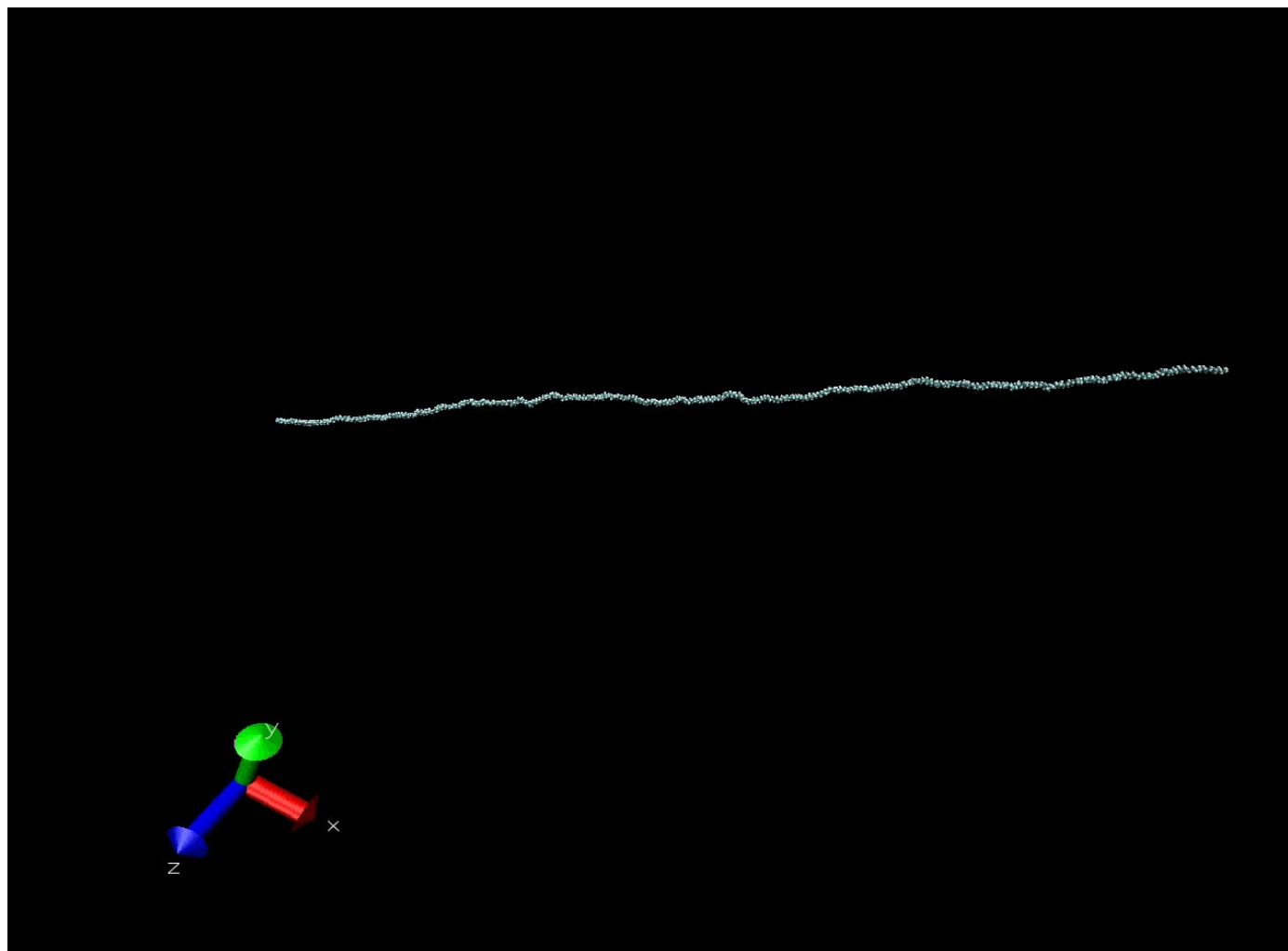
## Possible explanations of the rate constants increase with the chain length and change in the chain configuration

2. Chain stretching induced by bending vibrations.
  - Corrections to TST-based rate constants presented on the previous slide were obtained within a simple model that assumes uniform C-C bond stretching along the chain.
  - In reality, C-C bond stretching can be non-uniform, as illustrated here for a 100% extended chain:



## Possible explanations of the rate constants increase with the chain length and change in the chain configuration

2. Chain stretching induced by bending vibrations.
  - Non-uniform C-C bond stretching results in larger C-C bond scission rates closer to the ends of a 100% extended chain, as illustrated below:



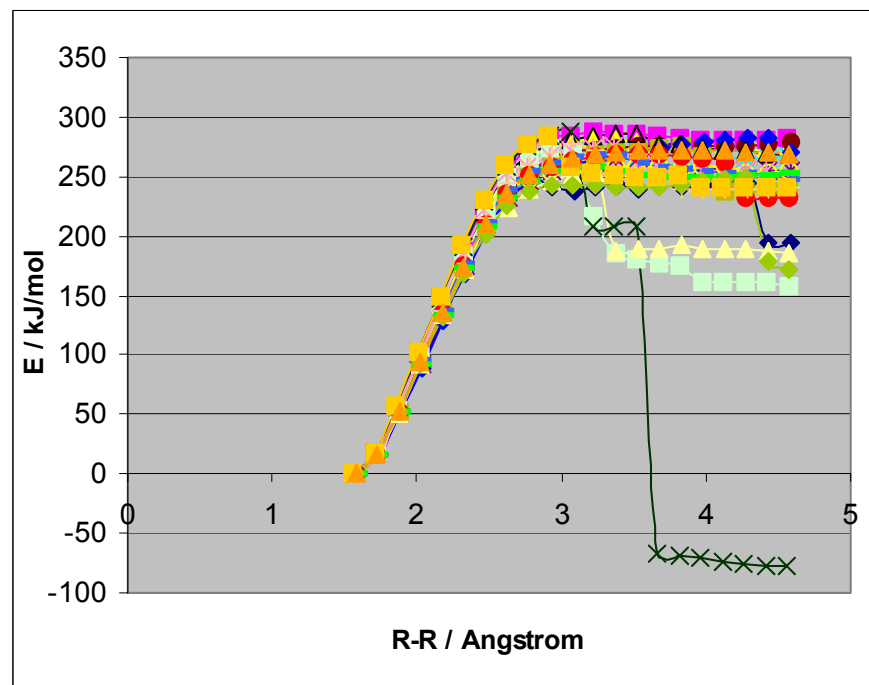
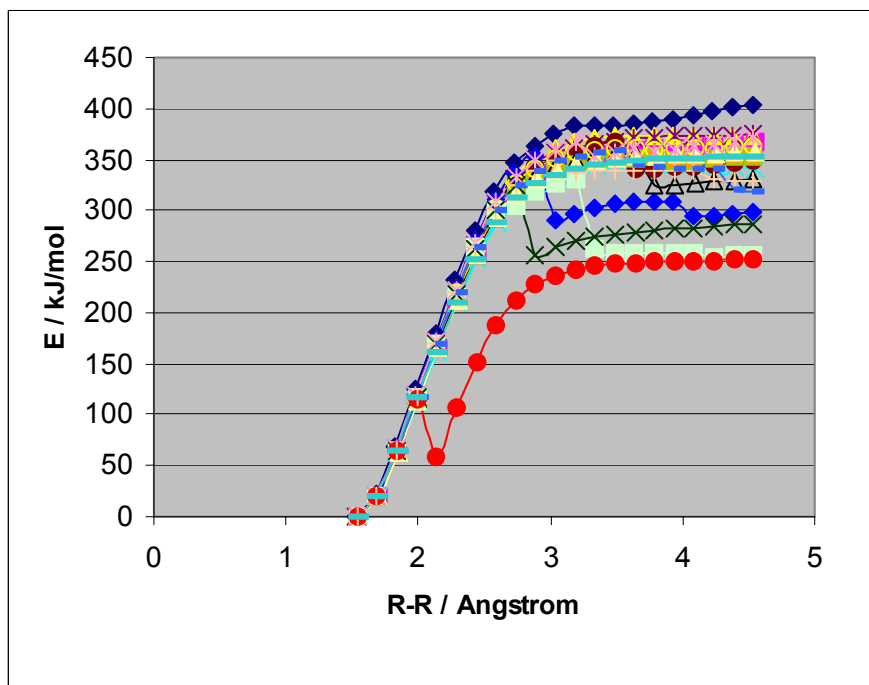
## Backbone C-C scission in condensed phase

- Nyden, Stoliarov, and coworkers (2004):
  - nonbonding interactions induce torsional and angular stresses; these stresses are larger in larger polymer molecules.
  - These stresses are partially relaxed when the polymer chain is broken, thus reducing the barrier for C-C backbone scission.
- Current work:
  - Potential energy surfaces of coiled PE-500 and PIB-300 were studied using molecular mechanics and quantum chemical methods.
  - The results demonstrate the existence of a distribution of effective activation energies for C-C backbone scission. Most C-C bonds in the backbone chain have bond strength values clustered around the C-C bond strength of an isolated prototype gas-phase molecule (e.g., n octane for PE). However, a fraction of bonds has significantly lower bond strengths (see next slide).



## Backbone C-C scission in condensed phase

- Current work:
  - Most C-C bonds in the backbone chain have bond strength values clustered around the C-C bond strength of an isolated prototype gas-phase molecule (e.g., n octane for PE). However, a fraction of bonds has significantly lower bond strengths.
  - These findings are in agreement with the earlier suggestion by Nyden, Stoliarov, and coworkers that relaxation of nonbonding stresses can reduce the barrier for C-C backbone scission.



## Summary

- Polymer backbone C-C scission reactions were studied computationally using polyethylene and polyisobutylene as prototypes.
- Molecular Dynamics calculations demonstrate that rate constants (per C-C bond) increase with the chain length and depend on the conformation of the molecule. Rate constants are significantly larger than predicted by Transition State Theory or from analogy with small alkanes.
- Nonuniform distribution of local temperatures was observed in MD simulations, which can partially explain rate enhancement.
- Partial chain stretching induced by bending vibrations was observed. This chain stretching results in reduction of the effective barrier for C-C bond scission. Calculated rate enhancements are in approximate agreement with those observed in MD simulations.
- Potential energy surfaces studies of coiled polymers demonstrate that relaxation of nonbonding stresses can reduce the barrier for C-C backbone scission, in agreement with earlier suggestion by Nyden, Stoliarov, and coworkers (2004).



## Acknowledgement

This research was supported by National Institute of Standards and Technology, BFRL, Fire Grants Program, under NIST grant No 70NANB4H1128.



THE CATHOLIC UNIVERSITY OF AMERICA